

THE NITROGEN CONTENTS

OF

COMMERCIAL DISTILLED WATER

By

WILLIAM CULLEN UHLIG, PH. B.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF
PURE SCIENCE OF COLUMBIA UNIVERSITY.

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INTRODUCTION.

The subject of this Dissertation was suggested by a paragraph in the Report for the Connecticut Agricultural Experiment Station for the year 1900. The Station had examined samples of all waters sold in Connecticut and had published the results of the analyses, with comments. Among the samples were three distilled waters and after tabulating the results the station commented on them as follows: "The variations shown . . . indicated a difference in the skill with which these waters were prepared, as well as a difference in the nature of the water used for distillation, and show that there is a great variation in commercial distilled water."

One reason why this work was undertaken was to try to discover what an analysis of distilled water means (following the usual methods for sanitary water analysis). The growing importance of distilled water as a commercial product, and the increasing number of distilled waters on the market, will soon make it necessary to have some method of analysis or interpretation of analysis in order to compare different distilled waters.

In the second place a number of States have pure food and drug laws in which the standard for drugs is the United States Pharmacopœia; distilled water in this connection is classed as a drug. The writer realizes that a water answering to a strict interpretation of all the tests of the Pharmacopœia is a commercial impossibility, and almost an impossibility even on a small scale; so, in this work, a comparison is made between commercial distilled water and distilled water prepared according to the Pharmacopœia.

In considering the constituents, as determined in a sanitary water analysis, we may assume at the beginning that the water must have no color, taste nor odor. Chlorine must be absent as its presence argues carelessness in distillation, or in other words some of the original water has been carried over, which takes the product out of the class, Distilled Water.

Solids will be present invariably. These come from the glass vessels in which the water is kept and transported, and also from dust gathered by the water in passing from one receptacle to another. They might be eliminated by substituting platinum or silver for glass and by taking extreme precautions in filling receptacles, but either would be prohibitory commercially. We may allow a distilled water to have not more than 10 parts per million total solids; of these solids not more than one half should be "Organic and Volatile." The amount of solids will be influenced by the age of the water, that is, the length of time it has been in glass.*

This leaves only the Nitrogen contents by which to judge the water. It is understood that in a distilled water Nitrogen as ammonia, nitrites or nitrates has not the same significance as the same constituent in a natural water. In fact it has no significance in respect to the healthfulness or deleteriousness of the water, but it is the only variable and consequently gives the only figures by which we can judge two waters comparatively. The writer has tried to discover under what conditions these Nitrogen containing compounds are produced and the possibility of eliminating them.

The water operated on was Croton water. The four stills used differed either in size or in position of heating surface; an outline description of each still is given before giving the results. Four runs were made with each still. The first run was with water alone, corresponding to the method of the Pharmacopœia. The second run was with Potassium Hydroxide in order to liberate the free ammonia quickly somewhat parallel to the analytical determination of free ammonia. The third run was with Potassium Hydroxide and Potassium Permanganate to parallel the determination of total (free and albumenoid) ammonia. These runs were all made from clean stills. The fourth run was made after running approximately 4000 Gallons from the Still after Run 3, in order to see the effect of the accumulated residues on the product.

The stills, which are of varying capacities, have a general resemblance, consisting of two cylinders, a larger below and a smaller above. The lower contains the heating coils and was

*Action of Water on Glass.—F. Foerster, Ber. 26. 2915-2922. Zeit. anal. Chem. 33. 322-335. E. Hoyer, Chem. Zeit. 22. 1033.

filled with the water to be distilled, while the upper contains two or three reboiling pans. The first steam condensed in the lowest pan, was reboiled by the steam passing into it, condensed again in the next pan, volatilized again and so on into the condenser. The coils were heated by steam at a gauge pressure of 70 lbs. corresponding to a temperature of 157°C . In every case 20% of the contents remained in the still at the close of the operation. The differences among the stills will be noted in the discussion of results.

The methods of analysis employed were the usual ones for sanitary water analysis. For the determination of Nitrites the Sulphanilic acid and Naphthylamine hydrochloride method was used; for Nitrates the Phenolsulphonic acid method. Determinations of free ammonia and of nitrites were made within three hours after the distillation; albumenoid ammonia and nitrates within twenty-four hours. The results are expressed as Nitrogen in parts per million.

ACKNOWLEDGMENT.

This work was undertaken with the approval of Professor Charles E. Pellew.

It is due solely to his consideration that it could be carried on and I take this opportunity to express my gratefulness for his kindness and interest. I wish also to extend my thanks to Mr. Arthur B. Park, M. E., for his invaluable assistance with parts of the work, and for his many suggestions.

WILLIAM C. UHLIG.

COLUMBIA UNIVERSITY,

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OPERATIONS.

STILL No. 1.

Holding contents 400 gallons. Output 320 gallons.

Type of still: Two cylinders, the upper very little less in diameter than the lower, and containing two reboiling pans. The heating surface consists of three spiral coils one above the other, each provided with valves allowing them to be shut off independently of one another. The top coil was uncovered after 181 gallons had been distilled; the second was uncovered after 266 gallons. The third was still covered when the total 320 gallons had been removed.

During the runs each coil was shut off as soon as the water reached that level. This still was fitted with inferior valves and the coil would remain hot, however, due to the valves not being absolutely tight. As will be seen this had an appreciable effect on the nitrogen contents of the output.

RUN No. 1.

The still was filled with croton water having the following nitrogen contents:*

Nitrogen as Free Ammonia,	.021
“ “ Alb. “	.117
“ “ Nitrites,	0
“ “ Nitrates,	.15

Sample 1— after 58 2 gallons or 14.55% of holding capacity.

“ 2— “	116.4	“	29.1 %	“	“
“ 3— “	174.6	“	43.65%	“	“
“ 4— “	232.8	“	58.20%	“	“
“ 5— “	291	“	72.75%	“	“
“ 6— “	320	“	80.00%	“	“

* The figures given for croton water were taken from the weekly reports of the New York Department of Health.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.061	.028	0	.025
" 2	.041	.015	0	.028
" 3	.026	.013	0	.027
" 4	.023	.018	.002	.025
" 5	.018	.021	.001	.024
" 6	.036	.051	0	.025

RUN No. 2.

The clean still was filled with croton water and 60 grammes of Potassium hydroxide added.

Nitrogen contents of water used :

Nitrogen as Free Ammonia,	.021
" " Alb. "	.128
" " Nitrites,	.0
" " Nitrates,	.15

The samples were taken at the intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.061	.025	0	trace
" 2	.048	0	0	"
" 3	.038	.016	0	.02
" 4	.046	.003	0	trace
" 5	.041	.006	0	"
" 6	.069	.013	0	"

RUN No. 3.

The clean still was filled with water and 60 grammes of Potassium hydroxide and 120 grammes of Potassium permanganate added.

Nitrogen contents of water used :

Nitrogen as Free Ammonia,	.021
" " Alb. "	.148
" " Nitrites,	0
" " Nitrates,	.175

The samples were taken at the intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.148	.029	0	.01
" 2	.118	.018	0	.01
" 3	.084	.02	0	.02

Sample 4	.084	.023	trace	.02
" 5	.066	.018	"	.02
" 6	.184	.043	.001	.03

RUN No. 4.

After Run No. 3 the still, without having been cleaned, was filled with water, KOH and KMnO_4 added and the water distilled off. This process was repeated until the still contained the concentrated residue from 4000 gallons. It was then filled with water and 40 grammes KOH and 80 grammes KMnO_4 added; the water was then distilled and samples collected.

Nitrogen contents of water used :

Nitrogen as Free Ammonia, .021

" " Alb. " .169

" " Nitrites, 0

" " Nitrates, .205

Sample 1- after 53.3 gallons or 13.32% of holding capacity.

" 2 " 106.6 " 26.65% " "

" 3 " 160 " 40 % " "

" 4 " 213.3 " 53.32% " "

" 5 " 266.6 " 66.65% " "

" 6 " 320 " 80 % " "

Nitrogen as Free Ammonia. Alb. Ammonia. Nitrites. Nitrates.

Sample 1 .234 .049 0 0

" 2 .163 .021 0 0

" 3 .151 .026 0 0

" 4 .128 .041 0 0

" 5 .168 .049 0 0

" 6 .332 .107 .006 0

STILL No. 2.

Holding capacity 375 gallons. Output 300 gallons.

Type of still: Two cylinders, the upper one having a diameter one half that of the lower and containing three reboiling pans. The heating surface consists, as before, of three coils with shut off valves. The top coil was uncovered after 225 gallons had been distilled; the second after 279 gallons; the third remained covered at the end of the operation. The procedure was the same as in still No. 1, that is the coils were shut off as soon as the water reached their level.

RUN No. 1.

The still was filled with croton water having the following Nitrogen contents:

Nitrogen as Free Ammonia, .016

“ “ Alb. “ .154

“ “ Nitrites, 0

“ “ Nitrates, .225

Sample 1— after 43 gallons or 11.46% of holding capacity.

“ 2 “ 86 “ 22.93% “ “

“ 3 “ 129 “ 34.40% “ “

“ 4 “ 172 “ 45.86% “ “

“ 5 “ 215 “ 57.33% “ “

“ 6 “ 258 “ 68.80% “ “

“ 7 “ 300 “ 80. % “ “

Nitrogen as Free Ammonia. Alb. Ammonia. Nitrites. Nitrates.

Sample 1 .117 .015 0 0

“ 2 .077 .008 0 0

“ 3 .054 .006 0 0

“ 4 .043 .008 0 0

“ 5 .063 0 0 0

“ 6 .038 .016 .001 0

“ 7 .067 .010 .002 0

RUN No. 2.

The still was filled with croton water and 60 grammes of KOH added.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .012

“ “ Alb. “ .140

“ “ Nitrites, 0

“ “ Nitrates, .25

Samples were taken at the same intervals as in Run No. 1.

Nitrogen as Free Ammonia. Alb. Ammonia. Nitrites. Nitrates.

Sample 1 .076 .025 0 0

“ 2 .013 .008 0 0

“ 3 .038 .003 0 0

“ 4 .034 .007 0 0

“ 5 .031 0 0 0

“ 6 .028 .001 0 0

“ 7 .030 .001 0 .04

RUN No. 3.

The clean still was filled with croton water and 60 grammes of KOH and 120 grammes of KMnO_4 added.

Nitrogen contents of water used:

Nitrogen as Free Ammonia,	.012
“ “ Alb. “	.115
“ “ Nitrites,	0
“ “ Nitrates,	.225

Samples were taken at the same intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.197	.051	0	trace
“ 2	.123	.021	trace	0
“ 3	.095	.030	“	0
“ 4	.092	.013	.001	.01
“ 5	.087	.023	.001	.015
“ 6	.107	.038	.002	.02
“ 7	.161	.031	.004	.03

RUN No. 4.

The method of procedure was the same as in Still No. 1; the still containing the residue from 4000 gallons before being filled. The charge was 40 gms. of KOH and 80 gms. KMO_4 .

Nitrogen contents of water used:

“ as Free Ammonia,	.012
“ “ Alb. “	.090
“ “ Nitrites,	0
“ “ Nitrates,	.2

The samples were taken at the same intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.306	0	0	0
“ 2	.189	.005	trace	0
“ 3	.165	.008	“	0
“ 4	.148	.025	“	0
“ 5	.153	.049	.001	0
“ 6	.201	.031	trace	0
“ 7	.255	.008	.003	.035

STILL No. 3.

Holding capacity 700 gallons. Output 560 gallons.

Type of still similar to still No. 1. Upper coil uncovered at

375 gallons; second coil at 498 gallons; third coil still covered at the end of the operation. The procedure was the same as in Still No. 1.

RUN No. 1.

The still was filled with Croton water having the following Nitrogen contents:

Nitrogen as Free Ammonia,	.012
“ “ Alb. “	.100
“ “ Nitrites,	0
“ “ Nitrates,	.175

Sample No. 1— after 70 gallons or 10% of holding capacity.

“ “ 2— “	140	“	20%	“	“
“ “ 3— “	210	“	30%	“	“
“ “ 4— “	280	“	40%	“	“
“ “ 5— “	350	“	50%	“	“
“ “ 6— “	420	“	60%	“	“
“ “ 7— “	490	“	70%	“	“
“ “ 8— “	560	“	80%	“	“

Nitrogen as Free Ammonia. Alb. Ammonia. Nitrites. Nitrates.

Sample 1	.092	0	trace	0
“ 2	.063	.001	0	0
“ 3	.056	.007	0	0
“ 4	.044	.003	0	0
“ 5	.048	0	0	0
“ 6	.067	0	0	0
“ 7	.053	0	0	.04
“ 8	.059	0	trace	.04

RUN No. 2.

The clean still was filled with Croton water and 100 gms. KOH added.

Nitrogen contents of water used:

Nitrogen as Free Ammonia,	.012
“ “ Alb. “	.111
“ “ Nitrites,	0
“ “ Nitrates,	.150

Samples were taken at the same intervals as in Run No. 1.

Nitrogen as Free Ammonia, Alb. Ammonia. Nitrites. Nitrates.				
Sample 1	.082	.044	0	0
" 2	.061	.012	0	0
" 3	.041	.016	0	0
" 4	.038	.015	0	0
" 5	.036	0	0	0
" 6	.039	0	0	0
" 7	.038	0	0	.03
" 8	.038	0	0	.04

RUN No. 3.

The clean still was filled with Croton water and 100 gms. KOH and 200 gms. KMnO_4 added.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .014				
"	" Alb.	"	.104	
"	" Nitrites,		0	
"	" Nitrates,		.175	

Samples were taken at the same intervals as in Run No. 1.

Nitrogen as Free Ammonia, Alb. Ammonia. Nitrites. Nitrates.				
Sample 1	.204	0	trace	0
" 2	.130	0	"	0
" 3	.099	.016	0	0
" 4	.100	0	.001	0
" 5	.100	.016	.001	0
" 6	.095	.015	.002	0
" 7	.102	0	.002	.02
" 8	.224	0	.007	.025

RUN No. 4.

The still contained the residue from 4500 gallons. It was filled with Croton water and 60 gms. KOH and 120 gms KMnO_4 added.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .016				
"	" Alb.	"	.098	
"	" Nitrites,		0	
"	" Nitrates,		.2	

The samples were taken at the same intervals as in Run No. 1.

Nitrogen as Free Ammonia.		Alb. Ammonia.	Nitrites.	Nitrates
Sample 1	.201	.049	0	0
" 2	.161	.026	0	0
" 3	.118	.035	0	0
" 4	.107	.041	0	0
" 5	.117	.033	0	0
" 6	.168	.049	.004	0
" 7	.178	.041	.003	.03
" 8	.188	.018	0	.025

STILL No. 4.

This still is a duplicate of Still No. 2 in every respect except heating surface. Instead of being heated by three separate coils it has one coil entering the side of the still, making three series of convolutions and leaving at a lower point; this arrangement necessitates heating the entire coil even after it's upper portion is uncovered. The highest point of the coil was uncovered after 218 gallons had been distilled. The charges were the same as in Still No. 2, so they will not be repeated.

RUN No. 1.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .014

" " Alb. " .08

" " Nitrites, 0

" " Nitrates, .2

Sample No. 1 after 50 gallons or 13.33% of holding capacity.

"	"	2	"	100	"	26.67%	"	"
"	"	3	"	150	"	40 %	"	"
"	"	4	"	200	"	53.33%	"	"
"	"	5	"	250	"	66.67%	"	"
"	"	6	"	300	"	80 %	"	"

Nitrogen as Free Ammonia.		Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.067	.031	.002	0
" 2	.051	.030	.003	0
" 3	.038	.020	0	0
" 4	.031	.020	0	0
" 5	.026	.008	0	0
" 6	.056	.030	0	0

RUN No. 2.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .012			
"	"	Alb.	" .061
"	"	Nitrites,	0
"	"	Nitrates,	.2

Samples taken at the same intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.082	.035	.001	0
" 2	.044	.007	trace	0
" 3	.038	.012	0	0
" 4	.023	.001	0	0
" 5	.021	.013	0	0
" 6	.041	.016	0	0

RUN No. 3.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .012			
"	"	Alb.	" .08
"	"	Nitrites,	0
"	"	Nitrates,	.2

Samples taken at the same intervals as in Run No. 1.

	Nitrogen as Free Ammonia.	Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.193	0	.002	0
" 2	.084	.015	.001	0
" 3	.056	.018	.001	0
" 4	.051	.023	.001	0
" 5	.122	.026	.005	trace
" 6	.189	.064	.007	.015

RUN No. 4.

Nitrogen contents of water used:

Nitrogen as Free Ammonia, .012			
"	"	Alb.	" .08
"	"	Nitrites,	0
"	"	Nitrates,	.175

Samples taken at the same intervals as in Run No. 1.

Nitrogen as Free Ammonia.		Alb. Ammonia.	Nitrites.	Nitrates.
Sample 1	.158	0	0	0
" 2	.120	.026	0	0
" 3	.105	.038	0	0
" 4	.102	.048	0	0
" 5	.283	.084	.006	0
" 6	.444	.133	.013	trace

DISCUSSION.

Free Ammonia.

RUN No. 1.

The discussion will be carried on in connection with the plates, the ordinates showing the amount of nitrogen in parts per million, and the abscissas showing percentage of water figured on the total capacity of the still. The nitrogen contents of the water used varied so little that its influence can be neglected in discussing results.

We note the similarity of the curves of stills Nos. 1 and 4, and also of Nos. 2 and 3. In fact there is great similarity among all the stills until about 40% of the water has been distilled off, but from this point the individuality of each still affects the result. Nos. 1 and 4 are the consistent ones, having a gradual decrease in the amount of nitrogen, and then a rise due, most probably, to decomposition of nitrogen containing bodies in the concentrated residue; this is of course accentuated in the case of No 4, owing to the exposure of superheated coil and the baking of residue on this.

In No. 2 we have a rise at about 50% followed by a sharp drop as soon as the top coil is shut off; the nitrogen falling to a minimum to rise sharply as soon as the second coil nears the surface.

In No. 3 the minimum is reached at 40% the rise continuing after the first coil is shut off, falling again when the second coil is shut off, with a final "concentration" rise not as abrupt as the others, this latter fact due most probably to the greater volume of water in this still.

It is difficult to discuss the production of Nitrogen as Free Ammonia in Run No. 1, as our knowledge of the composition of the original water is so limited. We know that solutions of

Ammonia salts on simple distillation yield varying quantities of NH_3 . H. C. Dibbitts* has reported some figures in regard to the "Dissociation of Ammonia Salts in Aqueous Solution," he having experimented with Ammonium Chloride, Nitrate, Sulphate, Oxalate and Acetate. Dr. G. Gore† in a paper entitled "Analysis of Drinking Water for Ammonia" says in his "Conclusions":—"Water containing even a small amount of Ammonia or its salts yielded much of its Ammonia by simple distillation, and did not require the aid of Carbonate of Sodium to liberate it unless salts of Alumina were present. The production of Ammonia by distillation with carbonate of sodium appeared to be due to the carbonate acting on Nitrogenous matter." In his summary he gives figures very much higher than those given by Dibbitts. The solutions he used were Ammonium Hydroxide, Carbonate, Chloride, Sulphate and Phosphate, and his figures varied from 20% NH_3 from Ammonium Hydroxide to 66% from Ammonium Carbonate. Ammonium Sulphate and Phosphate yielded each 50% of their NH_3 to the distillate.

H. C. Dibbitts‡ also published the results of his experiments on the "Decomposition of Ammonium Salts by Potassium and Sodium Salts," showing the loss of NH_3 from a solution of Ammonium Sulphate when heated with Potassium Chloride. J. W. Mallet§ says: "In the case of waters containing Urea and other aminated bodies such as the leucine and tyrosine occurring among the products of putrefactive decay, some ammonia is so easily formed from these substances by boiling with sodium carbonate, or even without this addition, that it is impossible to distinguish sharply between pre-existing "free" ammonia (of ammoniacal salt), and that formed by the action of alkaline permanganate, the so called "albumenoid" ammonia.

H. Blücher§ gives a long list of compounds which might be present in the natural water, and we can only infer that there must be interaction between some of these with the production of ammonia, or of compounds, readily decomposable, liberating ammonia.

* Zeit. anal. Chem. 1874- 395-408.

† Chem. News 1884- 182-186.

‡ Zeits. anal. Chem. 1876- 245-250.

§ Report of the National Board of Health, 1882-page 198.

§ Das Wasser, pages 120-124. See also Tiemann-Gärtner's Handbuch der Untersuchung der Wasser pp. 20-24.

We have in Run No. 1 the production of ammonia by dissociation of ammonium salts, by the action of metallic salts on ammonium salts, and lastly, by changes in nitrogenous compounds of organic nature. Ammonia from this last source we cannot estimate even roughly as we do not know the compounds which may be present. The figures for free ammonia from Run No. 1 are of interest as showing the large amount of ammonia produced and the rate of production.

RUN No. 2.

In discussing Run No. 2 (with KOH alone) if we contrast the figures with those from Run No. 1 we will notice in Still No. 1 that the Nitrogen in the first sample was the same in each case, but in the other samples the quantity in Run No. 2 was higher and the minimum point was just after the first coil was exposed, then there was a rise followed by a slight fall with a final abrupt rise after uncovering the second coil. In the other stills the results in Run No. 2 are all lower than in Run No. 1 which is contrary to what we would expect. From the figures we must infer that Stills Nos. 2, 3 and 4 represent normal conditions and that Still No. 1 is abnormal. From this we may conclude that on distilling water alone the greater bulk of the ammonia existing as ammonium compounds is given off and also a quantity of free ammonia or free ammonia producing substance is formed by interaction and decomposition of Nitrogen containing bodies existing in the water. The reaction of the distillate is acid due to Carbon di-oxide and large quantities of this gas are given off. In the case of the KOH distillation the alkalinity of the solution prevents or diminishes this decomposition of nitrogen containing bodies and most of the ammonia we get is that from already existing ammonium compounds. We notice in Run No. 2 in Stills Nos. 2, 3 and 4 a gradually diminishing ammonia contents until the last sample when there is a slight rise; this rise is more pronounced in Still No. 4 than in either of the others, and this can be explained by a resemblance between Stills Nos. 1 and 4. In Still No. 1 there is a diminishing curve for about one half the run, and from this point the curve becomes irregular. The steam coils in this still were fitted with inferior valves, and when the valves were shut off considerable steam still leaked through thus keeping the exposed coil at a high temperature.

The spray thrown on the coil was immediately evaporated leaving a residue of the solids from the water mixed with Potassium Hydroxide; this mixture at this temperature would liberate ammonia containing compounds.*

In Still No. 4 the whole coil is heated all the time, but the coil is placed lower in the still so the rise of the ammonia curve does not take place until further along in the operation, and the upper part of the coil being nearer the surface of the boiling water does not have the same opportunity to get so thoroughly dry as to accentuate the baking process to the same degree as in Still No. 1.

RUN No. 3.

In this run we get, for the first time, results in every case similar to those which we could have predicted; that is, a large quantity of nitrogen in the first sample, then a quick diminishing to the second and then a gradual falling off till we reach a minimum. At this point concentration begins to have an effect and we get a rapid rise of nitrogen in the final samples. This is especially noticeable in still No. 4, but contrary to expectation it does not take place in still No. 1 until after the second coil is exposed. There is nothing in the free ammonia in this run to merit special discussion.

RUN No. 4.

In this run the conditions are as follows: The stills contained in addition to the water, fresh Potassium hydroxide and fresh potassium permanganate, residual hydroxide and permanganate, oxides of manganese in various states of reduction, and the innumerable products resulting from the partial oxidation of the nitrogen containing compounds originally in the water. In this run we expect an increased yield of ammonia, as we have compounds more or less oxidized by the previous treatment, and the sum of their ammonia plus the free and albumenoid ammonia in the fresh water give the high figures recorded. The curves are exceedingly abrupt, descending in the first samples and ascending in the last. Again the parallel between stills Nos. 1 and 4 can be seen, the only discrepancy being the low figure for the first sample from still No. 4. This the writer cannot explain. Another noticeable

*Wanklyn, Water Analysis, 10th Edition, page 195.

feature is the comparatively low figures for the nitrogen in the first five samples from still No. 3, the amounts being not very much higher than those from run No. 3 of this still. This is due, in all probability, to the larger capacity of the still, and the greater bulk of liquid seems to affect the result, the dilution being the same. When the contents became more concentrated the greater part of the albumenoid ammonia was liberated suddenly (sample 6), and in the remainder of the run the curve is less abrupt than in any of the other stills.

Albumenoid Ammonia.

The term "Albumenoid Ammonia," as used in water analysis, is only a convenience; here it has the same significance, meaning ammonia obtained by distillation with alkaline permanganate. Any ammonia obtained in this manner from distilled water must be due to the decomposition of nitrogen containing compounds which are themselves volatile or volatile with steam. In run No. 1 we can assume that any "Albumenoid Ammonia" found already, existed as a volatile compound or such compound is formed by the heat of the operation.

In run No. 2 we have the same causes for the production of "Albumenoid Ammonia" as in run No. 1, but the results ought to be affected by the potassium hydroxide. We should have either an increased amount of "Albumenoid Ammonia," due to the above causes, plus other volatile "Albumenoid Ammonia" compounds formed by the action of KOH on other nitrogen containing bodies in the water, or less "Albumenoid Ammonia," due to the KOH acting on the previously existing volatile "Albumenoid Ammonia" compounds and changing them to some other forms. We find that the latter is the case with the single exception of still No. 3, and the greater bulk of water in the still may have some influence on this.

In run No. 3 we eliminate all previously existing "Albumenoid Ammonia," and all results we obtain must be from compounds formed during the reaction.

In run No. 4 we may expect the same results as from run No. 3, but with the quantities increased by the presence of partly decomposed and partly formed bodies, due to the accumulation of residues.

Run No. 1.—In this run in still No. 1 we have the nitrogen

figure gradually falling until the first coil is uncovered and rising from this point with a final concentration rise.

In still No. 2 the quantity is very small and the curve comparatively flat until about 50% of the water has been distilled. After this point the Albumenoid Ammonia disappears to reappear after the first coil has been uncovered. The concentration rise is larger in amount but it falls again before the greatest concentration is reached.

In still No. 3 we have peculiar results. The first sample contains no Albumenoid Ammonia; there is a slight amount in the second and the maximum is reached in the third, the down curve, not as abrupt as the up curve, disappears by the time 50% of the water has been distilled; there is no further production, the concentration rise being entirely absent. The state of dilution was the same in all the stills but the amount of water treated was greater in this still and this must be the factor affecting the result.

Still No. 4 shows results similar to still No. 1 except that the curve is flatter in the earlier stages of the run, and the minimum reached is lower; this last result is due, no doubt, to the different relative positions of the heating surfaces in each still. The similarity is due to the same causes mentioned in the discussion of free ammonia in these two stills.

Run No. 2.—In still No. 1 we have at first approximately the same amount of Albumenoid Ammonia as in run No. 1, but this is followed by a sample showing absence of Albumenoid Ammonia; then a rise followed by another fall and then a consistent rise to the end of the run.

In still No. 2 we have a larger amount in the first sample than in the corresponding sample of run No. 1. The next three samples approximate the same in the two runs, the Albumenoid Ammonia disappearing in the fifth sample, but in this run the concentration rise is very minute.

In still No. 3 we have the one case where the Albumenoid Ammonia is higher in run No. 2 than in run No. 1. There is a large amount in the first sample, then a sharp drop followed by a slight rise and then a drop to zero and no further appearance of albumenoid Ammonia.

In still No. 4 we have figures which may be compared with those from still No. 1, that is a fall then a rise, then a fall to a

minimum about the point of uncovering of heating surface and then a rise to the end of the run.

Run No. 3.—Stills Nos. 1 and 2 show a resemblance in this run; the amount of Albumenoid Ammonia is high compared to the previous runs, but the noticeable point is the undulating character of the curves. It would appear from this that the volatile compound which produces ammonia, when distilled with alkaline permanganate, is passing over with the steam continuously, but also a certain quantity is accumulating in the still and is liberated suddenly, and after an interval another quantity accumulates and is liberated; in other words some of the formation of volatile Albumenoid Ammonia producing compound is intermittent.

In still No. 3 we have very little Albumenoid Ammonia but that which is produced passes over in this intermittent manner.

Still No. 4 acts differently. In this run there is a very smooth curve from zero in the first sample through a flat curve to the fifth sample and then a sharp rise at the end.

Run No. 4.—In the beginning of this run we see a resemblance between Stills Nos. 1 and 3, and between Stills Nos. 2 and 4. Judging by the construction of the stills as long as all the heating surface is covered Stills Nos. 1 and 3 are identical in every respect except size, while Stills Nos. 2 and 4 are exactly identical, and the writer had expected to find resemblances between the members of each group and contrasts between the two groups, but here in the beginning of this run is the only place where this occurs.

Stills Nos. 2 and 4 have the upper cylinders much smaller in proportion to the lower (areas have the ratio 1:4) than have Stills Nos. 1 and 3 (No. 1 areas as 1:1.75. No. 3 areas as 1:1.9). In this run the water operated on had in solution a number of decomposition products and foamed much more than any previous run. In Stills Nos. 2 and 4 the foaming, when the water commenced to boil, carried to nearly the top of the still filling the reboiling pans with the solution in the still. This pair of stills have each three reboiling pans, and the amount of solution carried into each pan varied inversely as the height. When the water settled down to quiet boiling the volatile albumenoid ammonia compound was passed from one pan to the next, and in each pan it was acted on by the reagents and broken up am-

monia being liberated. This eliminated all albumenoid ammonia from the first sample but it also exhausted some of the permanganate in the reboiling pans. As the permanganate became exhausted more of the volatile compound passed over into the distillate until we reach a maximum, in Still No. 2, in the fifth sample; we may assume that the amount of the compounds, capable of producing this volatile body, in solution was becoming less, and so, in Still No. 2, there is a decrease from this point. A parallel point in Still No. 4 is about the fourth sample but here the effect of the exposed heated coil is apparent and we get a rapid rise due to the baking effect of the uncovered coil.

In Stills Nos. 1 and 3 we have the beginnings similar. There is no chemical reaction in the reboiling pans as the foaming not being constricted did not rise so high in the upper cylinder, and there being but two pans the lower is not as close to the surface of the water as in the other stills, so the first albumenoid ammonia compound formed or pre-existing in the water was volatilized or carried over by the steam before it could be attacked by the permanganate. As the operation went on the amount of this compound diminished showing, in Still No. 3, the undulations of the curve previously noticed, and finally in this still sinking to a minimum. In Still No. 1 we have a diminishing amount of albumenoid ammonia compound in the second sample, a slight rise in the third sample, but then when we ought to get another drop the effect of the heated coil is felt and we get a continued rise, though the undulating curve is still seen as the rise from the third sample to the fourth is much more abrupt than that from the fourth to the fifth and the final one is again abrupt.

From the time of Wanklyn's first paper on "Albumenoid Ammonia" in 1867 the identity of the compounds which give rise to this substance has been unknown. Wanklyn's first impressions of the "all-sufficing" qualities of this reaction have been modified until now the amount of "Albumenoid Ammonia" is only one of several factors used in judging a water. Wanklyn and his co-laborators tried the reaction on various nitrogen containing bodies and obtained varying results with different compounds. They found that some compounds gave off volatile substances which on redistilling with alkaline permanganate gave

more albumenoid ammonia. To quote Wanklyn's words:—"The conversion into ammonia of only half the nitrogen of so many of the natural alkaloids is an interesting fact. Some light is thrown on it by the example of narcotine, which, although it gives up all its nitrogen as ammonia, gives it up slowly, and by dint of putting back the distillate; it doubtless also yields part of the nitrogen as methylamine in the first instance. A careful examination of strychnine has disclosed a somewhat similar state of matters in the case of that alkaloid. Apparently, the missing half of the nitrogen in strychnine passes provisionally into the state of some volatile alkaloid."*

S. Hoogenwerff and W. A. Vandorp† some years later made experiments similar to Wanklyn's with results agreeing more or less with his, but neither Wanklyn nor these later investigators mention the strong probability of similar reactions occurring when the process is used in water analysis.

When J. W. Mallet made his investigation on "Methods for the Determination of Organic Matter in Potable Water" in 1881, he mentioned this probability. Under his direction Dr. Smart made a number of experiments similar to Wanklyn's, and showed in some cases the production of a volatile compound which yielded more ammonia when portions of the distillate were returned to the retort.‡ Mallet in his "Special Conclusions as to the Albumenoid Ammonia Process," says:—"There is evidence that in some cases nitrogenous organic matter is volatilized during the distillation for free ammonia, which, if it had been retained would have yielded up its nitrogen as albumenoid ammonia; not affecting the Nessler reagent, such nitrogenous matter escapes detection under either head."|| Thus calling attention to this probability.

Ira Remsen in a "Report on a Peculiar Condition of the Water of Boston in Nov. 1881," says:—"This clearly indicated that in the first stage of the process as usually conducted, there passed over with the free ammonia some nitrogenous substance capable of yielding ammonia with permanganate of potash."

*Water Analysis. 10th Edition, page 195.

†Berichte 1877, 1936-1939, 1878, 1202-1206, 1879, 158.

‡Report of the National Board of Health, 1882, pp. 252-257.

||Report of the National Board of Health, 1882, page 198.

Chas. W. Marsh in "Notes on the Ammonia Process for Water Analysis,"* calls attention to the same fact.

We may conclude from this investigation that the "Albumenoid Ammonia" compounds belong to, at least, two classes, volatile and non-volatile. We have some volatile on simple distillation, which appear to be unaffected or only slightly affected by potassium hydroxide. Then we have others formed during distillation with alkaline permanganate similar to the results in the experiments cited above; as these latter are formed by oxidation in the still we are justified in concluding that the already existing volatile compounds in the water were formed, from compounds similar to the latter, by natural oxidative processes.

Nitrites and Nitrates.

The discussion of the causes of the presence of nitrites and nitrates in distilled water presents no great difficulties. The quantities are small and in nearly every case the greatest amounts are toward the close of the run.

In Still No. 1, Runs Nos. 1 and 2, we have the only cases where the nitrates are persistent in approximately the same amounts throughout the entire run. We can suppose that this nitrate existed in the water, most probably as ammonium nitrate, and the salt was dissociated in the boiling and carried over with the steam. The smaller quantity in run No. 2 of this still is due to the reduction of some of the nitrates by the action of potassium hydroxide on the metal of the still;† and also to some of the nitrate combining to form potassium nitrate.

In Stills Nos. 2 and 3 in these runs we have the nitrites and nitrates appearing only at the close of the run, and this would tend to show that some nitrogen is oxidized and liberated when the still contents get concentrated.

In Still No. 4, Run No. 1, we have some nitrites in the first two samples due to dissociation, and in Run No. 2 a less quantity in the corresponding samples, some having been eliminated by reduction.

In Run No. 3 in all the stills we have the greatest production of both forms of oxidized nitrogen, and we would expect this from the oxidation in this run. As the concentration in-

*Chem. News, 1883, 19-20.

† Leeds, Zeit., Anal. Chem., 1879, 428-430.

creases so does the amount of oxidized nitrogen; this is partly an oxidation of ammonium salts, and from the high ammonia content of this run we would expect a high nitrogen oxide content.

In Run No. 4 we have a still more vigorous oxidation but a falling off in nitrous and nitric oxides. This may be explained by the quantity of permanganate present, a large amount of alkaline permanganate acting on ammonium compounds giving nitrogen gas, while a less amount gives partly nitrogen and partly nitric acid.*

In these runs we again notice the increase of nitrogen with the increase of concentration. As dilution is favorable to dissociation we must conclude that this oxidized nitrogen, in most cases, does not exist as such in the water but is formed during the process, concentration evidently contributing to its formation.

NOTES ON THE ANALYTICAL OPERATIONS.

The quantity used for the estimation of the ammonias was 500 c.c. In a few cases all the free ammonia came over in three tubes (50 c.c. each), while in three cases it required nine tubes to bring over all the total ammonia; these three cases were all from Run No. 4, being samples 1 and 6 from Still No. 1, and sample No. 6 from Still No. 4. The average was less than six tubes.

The difficulty, noticed in determining total ammonia in some natural waters, of getting a sharp end point on account of the ammonia coming over indefinitely was entirely absent, as the color in each tube was noticeably less than that in the preceding one and the final tube was invariably without color.

In several instances the total ammonia (the sum of the free and albumenoid ammonias) was less than the free ammonia. In two instances the figures were rejected on this account and some more of the sample analyzed but with the same result. This is probably due to oxidation of the ammonia. This explanation has been suggested by Tidy† in his objections to the Wanklyn process

* Wanklyn, Jour. Chem. Soc., 1868.

† Jour. Chem. Soc., 1879, 57.

The free ammonia distillates from Still No. 4, Run No. 2, gave a greenish color with Nessler reagent. Dr. Smart in the analysis of natural waters claims that this is an indication of decomposing organic matter of vegetable origin. As the organic matter of croton water is largely of vegetable origin we may infer that the compound producing this peculiar shade was carried from the still with the steam into the condensed water, and then again from the distilling flask into the Nessler tube. The quantity may have been increased or diminished in this double distillation but as we know nothing of the constitution of this body we cannot determine this.

THE CONDITION OF FREE AMMONIA.

In another series of experiments samples were collected and 50 c.c. Nesslerized direct, and then another portion of the sample analyzed for free ammonia. The following results were obtained:

RUN "A."			
Sample.	Reaction with Nessler Reag.	Free Ammonia.	Ammonia in 50 c.c.*
3	Ammonia free	.178	.009
4	" "	.112	.0056
5	" "	.02	.001
6	" "	.014	.0007
7	" "	.032	.0016
8	" "	.076	.0038
9	" "	.08	.004
10	" "	.094	.0047
RUN "B."			
6	" "	.068	.0034
7	" "	.073	.0036
8	" "	.112	.0056
9	" "	.102	.0051
10	" "	.128	.0064
RUN "C."			
4	" present	.166	.0083
5	" trace	.146	.0073
6	" free	.116	.0058
7	" "	.108	.0054

* The figures in this column were obtained by dividing the amount of ammonia by 20.

Sample.	Reaction with Nessler Reag.	Free Ammonia.	Ammonia in 50 c.c.
8	Ammonia free	.102	.0051
9	“ “	.074	.0037
10	“ “	.094	.0047
11	“ “	.108	.0054

RUN “D.”

7	Ammonia present	.174	.0087
8	“ “	.124	.0062
9	“ “	.106	.0053
10	“ “	.162	.0081
11	“ “	.112	.0056

These runs were made earlier than the preceding ones for the purpose of obtaining an ammonia free water, and no account was taken of the nitrogen contents of the water used and no attention was paid to the relative position of the heating surface to the level of the water in the still. The first 12 or 15% of the distillate was rejected before sampling, and the samples were taken at very short intervals, so, the conditions being different, there can be no comparison of curves to the curves of the runs already discussed.

Run “A.” was with potassium hydroxide and Run “B.” with potassium hydroxide and potassium permanganate, both runs being made in Still No. 1. The samples were Nesslerized and all rejected which showed a reaction; those which showed no reaction were analyzed for free ammonia. The results were so much higher than had been expected that two more runs were made on a different still (Still No. 2), and in Run “C.” the last two samples which showed a reaction with Nessler reagent were analyzed in addition to those which reacted ammonia free; in Run “D.” every sample showed a reaction so the last five were taken for analysis.

In Run “A.” we have a set of tubes containing from .0007 to .009 part of nitrogen as ammonia; in Run “B.” from .0034 to .0064, and in Run “C.” from .0037 to .0058, all reacting ammonia free. In the analysis of a potable water we use a standard ammonia solution containing .01 part of nitrogen per cubic centimeter and we can see and compare the color produced by Nessler reagent in 50 c.c. of water containing 0.1c c. of this solution, so all of the above amounts should be shown by the reagent; the figures for Run “A.”, Sample No. 6 (.0007) are

less than our smallest standard, but the color produced by this amount of ammonia, when compared with an ammonia free water containing an equal amount of the reagent, is easily discernable. From this we would infer that the ammonia in distilled water is there not all as ammonium hydroxide or ammonium salt but partly combined with some organic combination. This view is strengthened if we compare the figures of the first two samples of Run "C." and all the samples from Run "D." with those already mentioned. We have from .0053 to .0087, part all showing a reaction for ammonia; these are all less than the largest amount (.009) not reacting, and the one showing a trace (Run "C.", sample No. 5) contains less ammonia than some samples showing no ammonia reaction, and more ammonia than three samples in Run "D.", which gave a decided reaction. Run "D." never reacting ammonia free contains less ammonia in its minimum sample than do two of the samples which did not react, and approximately the same amount (within .0005) as seven of the nonreacting ones.

The figures obtained in this series would indicate that "Free Ammonia" exists in distilled water in two forms, one in inorganic combination reacting with Nessler reagent, and the other in organic combination not reacting with the reagent. The water in Runs "A." and "B." and the "ammonia free" samples of Run "C." contains only the "organic combination" ammonia, while that of the first two samples of Run "C." and all of Run "D." contains ammonia, most probably, in both combinations.

THE INFLUENCE OF TIME ON THE NITROGEN CONTENTS OF DISTILLED WATER

A sample of water was drawn directly from the condenser and the nitrogen determined. The demijohn was corked and determinations were made at intervals of one week.

Nitrogen as Free Ammonia. Alb. Ammonia. Nitrites. Nitrates.

Water freshly distilled, .174	.096	.007	.09
" at end of 1st week, .198	.216	.002	.03
" " " " 2d " .162	.028	.002	.06
" " " " 3d " .160	.066	.002	.03
" " " " 4th " .158	.036	.002	.025
" " " " 5th " .154	.018	.002	.045
" " " " 6th " .150	.026	.002	.125

It will be noticed that the free ammonia increased during the first week and then there was a gradual disappearance. Albumenoid ammonia increased in the first week and then diminished markedly at the end of the second week ; from this time it varied both up and down its main direction being toward disappearance. Nitrites diminished in the first week but at the end of this period they remained constant during all the time the water was under observation. Nitrates were high in the original water falling at the end of the first week but finally showing a strong tendency to increase until in the last sample they were very high

The first process seems to have been one reduction indicated by an increase in free ammonia and a decrease in oxidized nitrogen. After this we have a gradual decrease of free ammonia but not a corresponding increase in oxidized nitrogen. The general opinion is that free ammonia is gradually oxidized to nitrate, but, according to these results, there must be other causes acting on the formation of nitrates as we have not the rise of nitrate corresponding to the decrease in free ammonia, and the writer can explain this only by supposing that we have both oxidation and reduction going on together; oxidation of free ammonia to nitrate and reduction of nitrate to some other form than ammonia. The nitrite remaining constant would seem to indicate that this form of oxidized nitrogen acts as an intermediary between ammonia and nitrate, and between nitrate and the other reduced form and so remains in constant quantity.

The Albumenoid Ammonia figures are difficult to understand, Mallet and Smart* in their experiments on the "Change of Organic Matter on Keeping," obtained results, on different samples of water, somewhat similar to the above, that is, in some cases albumenoid ammonia increased in others it diminished, and they conclude that the Organic Nitrogen is in general being converted into ammonia and ultimately into nitrate. Unfortunately they did not determine the amount of nitrate, in fact, they base their conclusion on a few qualitative tests for nitrites.

Mason† divides nitrogenous organic matter in water into two classes. 1st. That which is easily acted upon by alkaline per-

* Report Nat. Board of Health, 1882, pages 243-249.

† Examination of Water, 2nd edition, page 75.

manganate solution. 2nd. That which is more stable, and from which no ammonia is evolved during distillation with the above reagent. He then says: "Upon standing for any considerable time this latter class becomes slowly converted into the less stable variety, which in its turn is gradually converted into "free ammonia," the ammonia in turn becoming finally nitrified, as already stated." He gives as reference the report of Mallet and Smart mentioned above.

In this connection it must be remembered that in a distilled water we have different conditions from a natural water. There is absence of the normal water bacteria whose function is nitrification, so it is unfair to apply the same reasoning to the discussion of the changes in this water as have been applied to the discussion of changes in natural water.

In this water we have the quantity of albumenoid ammonia rising and falling from week to week suggesting an analogy to the sinuous curve of the albumenoid ammonia produced in Runs Nos 3 and 4. This is interesting but it does not explain what becomes of the albumenoid ammonia unless we can suppose the existence of a compound intermediate between the albumenoid ammonia and the oxidized nitrogen. It will be noticed that in every case, except one (at the end of the 4th week), as the albumenoid ammonia rises the nitrates fall, and vice versa. We can assume that the albumenoid ammonia containing bodies exert a reducing action on the nitrates with the formation of an intermediate compound, and that some of the nitrogen is being stored up in this compound. Ultimately this nitrogen is oxidized to form nitrate as shown by the increase in nitrates at the end of the 6th week; also some albumenoid ammonia is converted into free ammonia and oxidized to nitrate as in natural water.

This will necessitate supposing Nitrogen in at least six combinations in the water. 1st. Nitrogen as free ammonia. 2nd. Nitrogen in organic combination which by decomposition will produce an Albumenoid Ammonia compound. 3rd. Nitrogen in Albumenoid Ammonia compounds. 4th. Nitrogen in unknown combination produced by interaction between Albumenoid Ammonia compounds and oxidized nitrogen. 5th. Nitrogen in Nitrites. 6th. Nitrogen in Nitrates. The 4th form is extremely hypothetical but it seems to be the only means of explaining the changes in the nitrogen contents of this water on keeping.

In general we may say that in distilled water, as in natural Water, the tendency is for the Ammonias to disappear and the Nitrates to increase.

COMMERCIAL DISTILLED WATER OF VARIOUS TYPES.

	No. 1.	No. 2.	No. 3.	No. 4.
Total solids,	7.2	5.0	5.0	4.5
Inorganic,	5.5	2.5	2.7	2.3
Organic and volatile,	1.7	2.5	2.3	2.2
Chlorine,	1.9	1.8	0.7	0.4
N as free ammonia,	.082	.272	.054	.095
" alb. "	none	.033	.038	.062
" nitrites,	none	none	trace	trace
" nitrates,	.075	.05	.038	.05

The four samples above represent four different types of distilled water. Of Nos. 1 and 4 the writer can speak from personal knowledge of the process used, while of the other two samples the process is surmised as admission to the factories was refused.

No. 1 is made from steam direct from the boiler; the steam is passed through a coke chamber and then into the condenser. The condenser consisted of a long vertical water-cooled pipe open at each end, the principle being to condense the steam to water at about 200-° 210° F., and the gases (CO_2 , NH_3 , etc.) are supposed to escape at the upper end of the condenser, while the water is drawn off at the lower end. The water is then passed through another coke chamber and finally through a strainer, to remove coke particles, etc., to a cooling system. The relatively high total solids are due to the solvent action of the hot water on the coke, and the chlorine is due to NH_4Cl dissociated at boiler temperature and pressure and carried over with the steam. Free ammonia persists notwithstanding the high temperature of condensation, while the absence of albumenoid ammonia and nitrites, and the relatively high nitrates may be explained by the age of the sample, as it was at least two weeks between distillation and analysis.

Sample No. 2 was from the æsthetic standpoint the least desirable water as it contained a sediment composed largely of

coke dust and pieces of rubber. From the behavior of the total solids on ignition it could be inferred that the water was condensed exhaust steam; at the moment of ignition there was formed a ring of carbon around the interior of the platinum dish at about the height of the original level of the water in the dish. This looks very much like light lubricating oil in the water, and the presence of coke dust argues a coke filter, but the filter failed to remove all the oil; the rubber was most probably disintegrated packing. As the water was cool when filtered it did not have any material solvent action on the coke so the total solids are not high. Chlorine is high for the same reason as in the previous sample, and ammonia is bound to be high because the first distillates are not rejected and the residues remain in the boiler indefinitely.

No. 3 is a water about the manufacture of which the writer was very anxious to learn but it was impossible to obtain access to the factory. By examining the exterior and chiefly by a knowledge of the other business carried on at the place of manufacture, distilled water being only an incidental, the process is supposed to be as follows: live steam direct from the boilers is used for heating purposes and instead of being returned to the boilers it is condensed and the water is put into some form of still and redistilled; the first distillate is, most probably, rejected and the balance collected. The water is thus twice distilled, the result of the first distillation being to break up some of the organically combined ammonia so that it is more liable to pass off in the first samples from the second distillation. The water still contains some ammonia of each kind; there is a small quantity of chloride but total solids and nitrates are low.

No. 4 is a straight distilled water made in a still somewhat similar to the stills on which these experiments were conducted, the first 15% rejected, the balance up to 80% being collected. Nitrogen is present in average quantities in both ammonias and in nitrates, but the total solids are low and chlorine is practically absent, as we can allow silver nitrate corresponding to this amount of chloride to change the indicator.

The nitrogen contents of all these waters show the impossibility of eliminating nitrogen from a distilled water, and also confirm the results of the foregoing experiments. These samples are not strictly comparative on account of the uncertainty

of the age of the samples. They were all bought from dealers and we have no way of knowing how long they had been distilled. No. 1 is probably the oldest as it was shipped from some distance out of the city, but the age of the others is uncertain.

AQUA DESTILLATA, U. S. P.

The object of inserting this section was to determine if a commercial distilled water fulfils the requirement of the United States Pharmacopoeia.

The method given by the Pharmacopoeia for the preparation of Distilled Water is as follows : Water, one thousand volumes, to make 800 volumes. Distil the water from a suitable apparatus provided with a block-tin or glass condenser, Collect the first 100 volumes, and throw this portion away. Then collect 800 volumes, and keep the Distilled Water in glass-stoppered bottles, rinsed with hot distilled water immediately before being filled."

The quantity taken was two Liters. The first 200 c.c. were rejected and the next 1600 c.c. kept as "Aqua Destillata." The method was as above except the flask was connected with a silver condenser. The water used was Croton water.

The Distilled Water gave a reaction with Nessler reagent. On analysis it showed the following Nitrogen contents :

Nitrogen as Free Ammonia, .054			
"	"	Alb.	" .016
"	"	Nitrites,	trace
"	"	Nitrates,	.03

The nitrogen contents of this water are slightly lower than in commercial distilled water, though the nitrogen contents will be affected by the quality of the water taken for distillation, and may vary within wide limits and yet be strictly in accord with the requirements of the Pharmacopoeia, so we can say that Commercial Distilled Water is "Aqua Destillata, U. S. P." in regard to Nitrogen contents.

Chlorides and Total Solids were not determined because we know that commercial distilled water can be prepared Chloride free, and we also know that we cannot keep a water free from inorganic solids even if we can prepare one free from organic solids which is doubtful.

The requirement "When 1000 c.c. of Distilled Water are evaporated on a water-bath to dryness, no residue should remain," is an impossibility when the water has been stored in glass. Water prepared according to the Pharmacopoeia will not fulfill this condition and consequently this must be modified. In the absence of an official maximum for total solids we are justified in assuming one ; the writer thinks that 10 parts per million is a fair limit and consequently, Distilled Water containing total solids less than 10 parts per million and otherwise having the properties of distilled water mentioned in the Pharmacopoeia is "Aqua Destillata, U. S. P."

CONCLUSIONS.

We may conclude from the results of the foregoing operations that commercial distilled water contains nitrogen in most cases in greater quantities than in the original water.

This is a fact usually overlooked by chemists, for though we occasionally come across some mention of it we are also liable to find some later investigator qualifying or explaining the reasons for the first ones remarks. Thus, Leeds* found fourteen times as much ammonia in distilled water as in the original used, but Mallet† comments on this saying, "taking doubtless the early portions of the distillate."

The literature on the subject of distilled water is very scanty, all references being scattered through papers on other subjects with incidental mention of distilled water. König in his exhaustive work on Water Purification treats the subject of distilled water with very few words. He says: "Da, wo Meerwasser die einzige Wasserversorgungsquelle bildet, wie z. B. auf Seeschiffen, muss dasselbe vorher durch Destillation trinkbar gemacht werden."‡ He goes on to say that water is boiled in one part of the apparatus and condensed in the other, and then with mention of two manufacturers of apparatus for water distillation he dismisses the subject.

It will be noticed that while water prepared on a laboratory scale can be made with almost total absence of nitrogen it cannot be done on a commercial scale. The bulk seems to affect the rate of production and we never get even a portion of nitrogen free.

The factors which determine the amount of nitrogen in distilled water are very numerous. It is influenced by the composition of the water used, the process, the type of still, the arrangement of heating surface, the temperature, the amount of water treated, the concentration, the accumulation of residues, and the age of the sample.

* Zeit. anal. Chem. 17, -276.

† Report Nat. Board of Health, 1882, -249.

‡ Die Vereinigung der Gewässer, Dr. J. König, Vol. I, p. 191.

There are two types of processes of which nothing has been said. One the distillation of water from an acidified solution is impractical from a commercial standpoint on account of the action of the acid on the metal of the still. The other, the continuous feed process, was not considered because the yield of ammonia is always high owing to the continuous fresh supply of ammonia containing water, and also to the accumulation of residues.

The nitrogen in distilled water has no effect on the physical properties of the water, and the only case in which it would be harmful from the chemical standpoint is in water analysis. In regard to its physiological effects we may say it has none, as the quantities though comparatively high are in reality extremely minute. The nitrogen may have some bearing in a biological sense in affecting the keeping qualities of the water on account of its influence on bacterial and fungus growths in the water.

Water after having been kept for some time in closed vessels at the proper temperature will develop an offensive odor. This is noticed with natural water only on shipboard as this is about the only place where water is kept in closed vessels for any length of time. Distilled water will also in a few cases, develop this offensive odor after standing, but the water must have been contaminated and the temperature must be suitable for the development of the organism. The nitrogen contents of the water must have some influence on this bacterial growth or the organism must draw its nitrogen from the air, which is unlikely. The determination of the conditions favorable to this growth would throw light on the role that nitrogen plays in distilled water, and would enable us to use the figures for nitrogen as shown by analysis to judge at least of the keeping qualities of the water. This is a subject for an investigation of a different character.

In the light of present knowledge the figures for nitrogen are of very little value in judging a distilled water. This leaves only the Chlorine and the Total Solids upon which to form an opinion of the water.

In comparing Distilled Waters the consideration of physical properties is important. These properties in connection with chlorine and solids determine which is the best water, supposing of course the nitrogen is within reasonable limits. We may say

that the water must be colorless, odorless and tasteless, with chlorine absent and total solids less than 10 parts per million. In this connection the use to which the water is applied has some bearing ; if for drinking the absence of color and the so-called "Blasengeruch" and "Blasengeschmack" is most important, and if for chemical purposes the minimum of total solids is to be desired.

A distilled water corresponding to to the above standard will satisfy the requirements of the U. S. Pharmacopoeia as nearly as they can be satisfied by any water.

BIOGRAPHICAL.

William Cullen Uhlig entered the Course in Analytical and Applied Chemistry, School of Mines, Columbia University, in October, 1892, and received the degree of Ph. B. in June, 1896. Registered under the Faculty of Pure Science of Columbia University as a candidate for the degree of Doctor of Philosophy in October, 1902, and studied under that Faculty to date.

PLATE I. RUN I. Free Ammonia

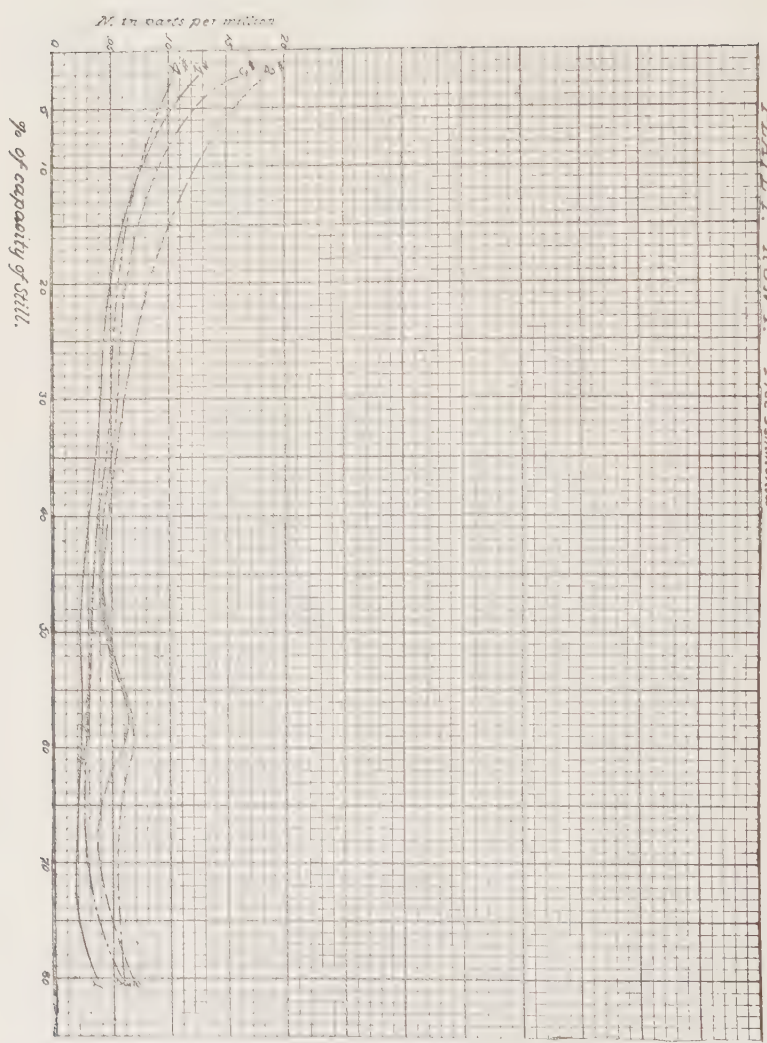


PLATE II. RUN II. Free Ammonia

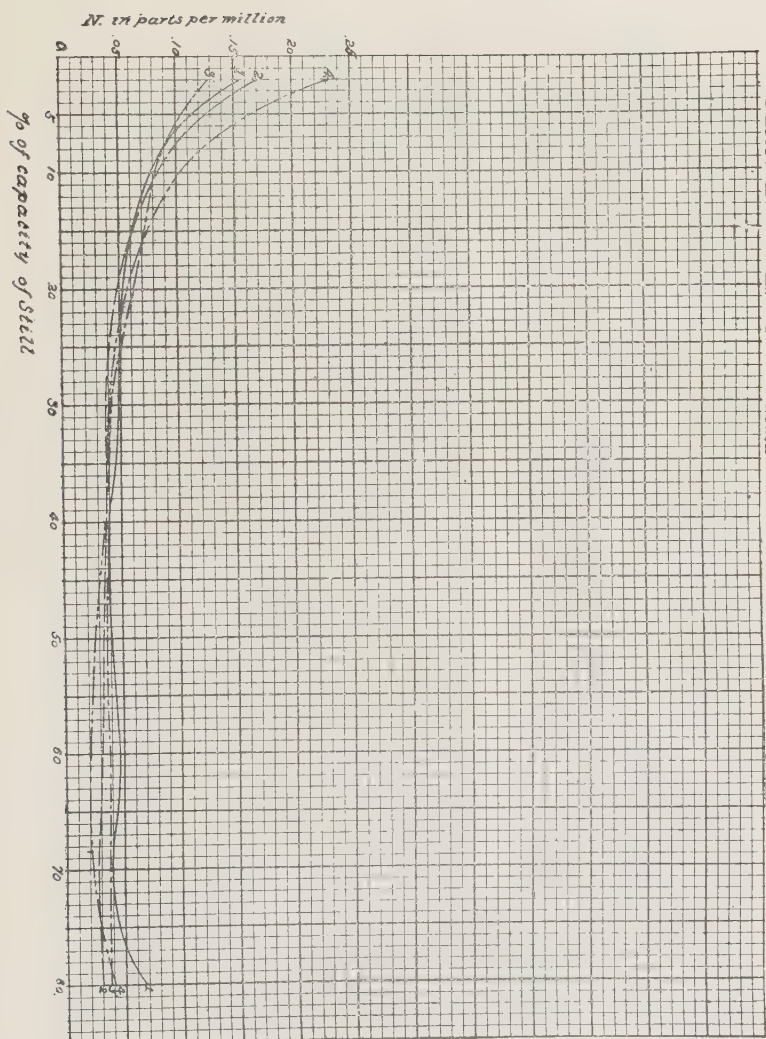


PLATE III RUN III. Free Ammonia.

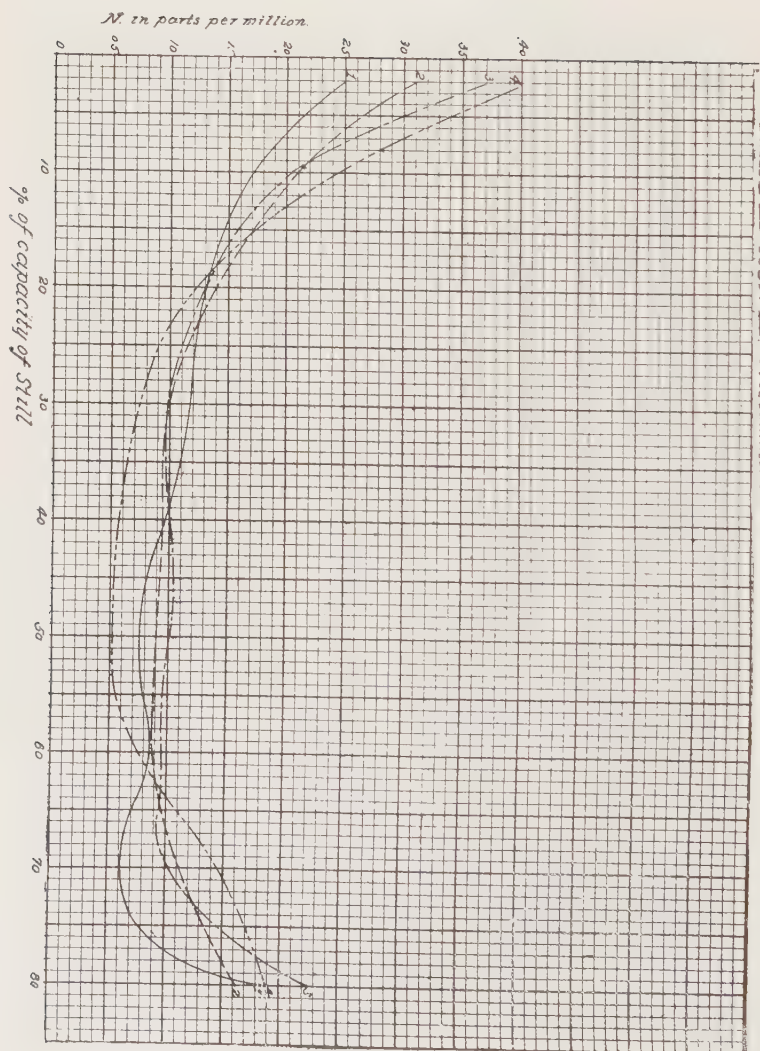


PLATE IV. RUN IV

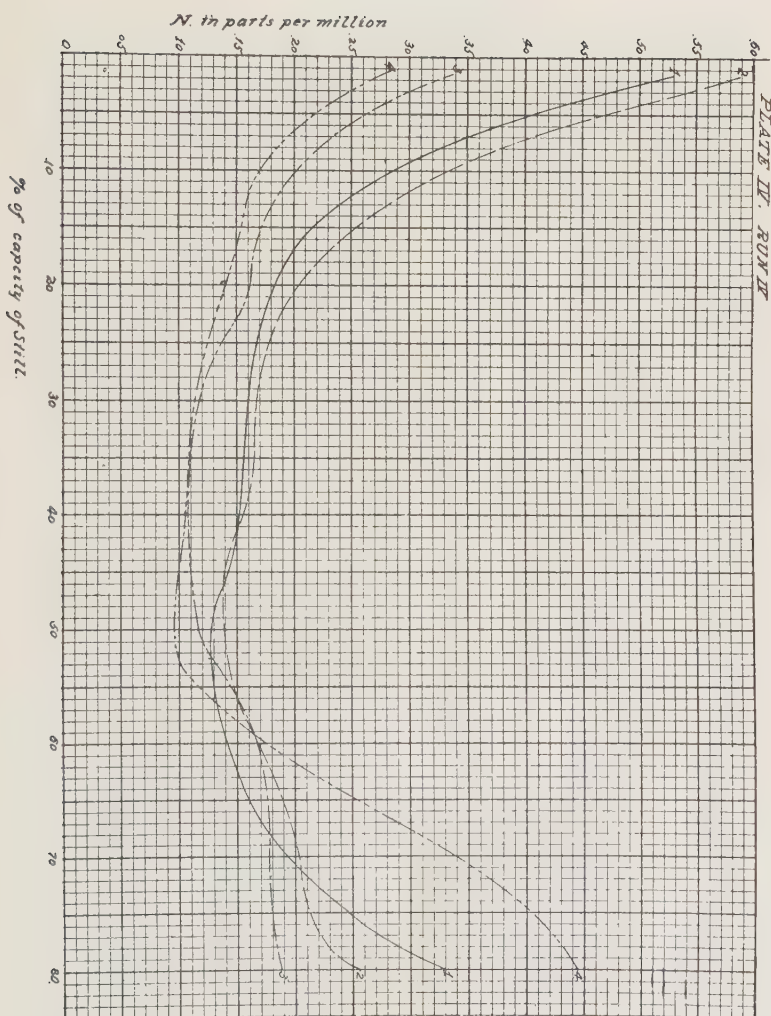
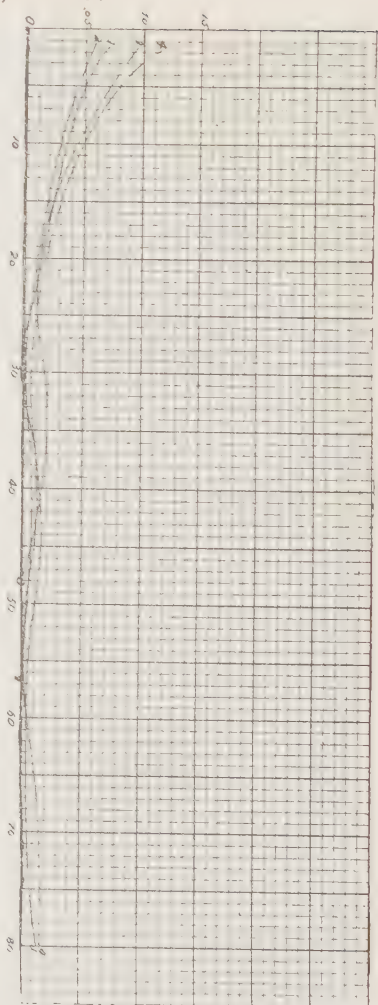
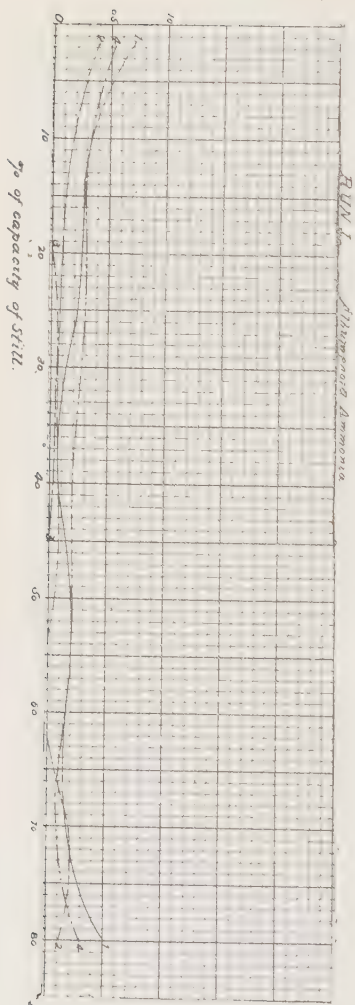


PLATE V. RUN II. Alluvial Ammonia

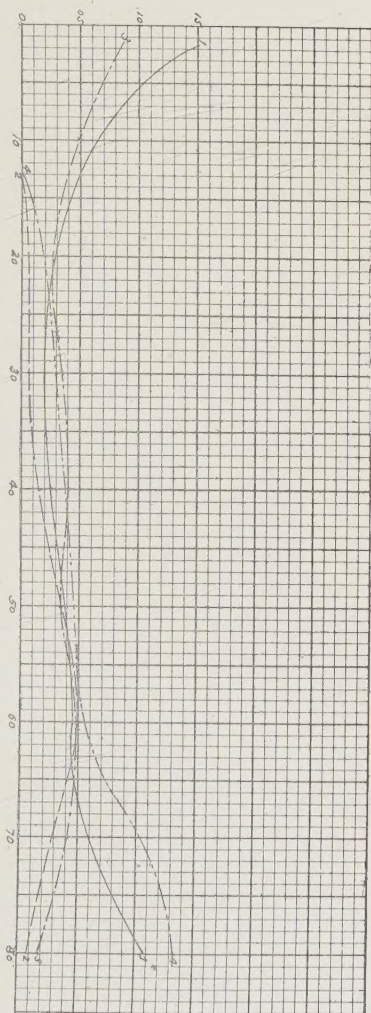


N in parts per million



% of capacity of still.

PLATE III. RUN IV. Albumenoid Ammonia



RUN III. Albumenoid Ammonia

